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SECOND QUARTERLY TECHNICAL REPORT

Report Date: November 30, 1962

August 1, 1962 to November 1, 1962.

"VARIABLE ENERGY GAP DEVICE"

CONTRACT NR. DA-36-039-SC-89106

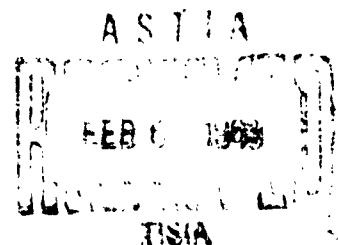
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DA36-039 sc-89106
Eagle-Picher Company

2nd Quarterly Report
1 August - 1 November 62

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SECOND QUARTERLY TECHNICAL REPORT

Covering the Period -

August 1, 1962 to November 1, 1962

Report Date: November 30, 1962

"VARIABLE ENERGY GAP DEVICES"

Order No. 1208-PM-62-93-93 (4912)

Date of Contract: May 1, 1962.

Amount of Contract: \$34,791.00

Contract Number: DA-36-039-SC-89106.

Report Prepared By:

L. E. Stone

Geo. N. Webb

Edited By:

J. R. Musgrave

**The Eagle-Picher Company,
Research Laboratories,
Miami, Oklahoma.**

The work performed under this Contract was made possible by the support of The United States Signal Research and Development Agency, Fort Monmouth, New Jersey.

TABLE OF CONTENTS

	<u>PAGE</u>
I. PURPOSE,	1
II. ABSTRACT,.	2
III. PUBLICATIONS, CONFERENCES AND REPORTS,	3
IV. FACTUAL DATA:	
A. Introduction,.	4
B. Fabrication:	
(1). Sequence of Fabrication,.	6
(2). Chemical Polish,.	7
(3). Phosphorus Diffusion,	7
(4). Zinc Diffusion,	9
(5). Contacting,	9
C. Studies and Evaluation:	
1. General,.	10
2. Carrier Concentration and Junction Depth,	11
3. Photovoltaic Parameters,.	14
4. Diode Characteristics,.	16
5. Spectral Response,.	16
D. Gallium Phosphide Synthesis,	19
E. Epitaxial Growth,.	25
V. SUMMARY AND CONCLUSIONS,.	30
VI. FUTURE STUDIES,	31
VII. REFERENCES,	32
VIII. PERSONNEL,	33

LIST OF TABLES AND ILLUSTRATIONS

	<u>PAGE</u>
Table I. Cell Fabrication Steps and Sequence,	6
Table II. Phosphorus Impurities from Emission Spectroscopy Analysis,.	7
Figure 1. Surface Resistivity as a Function of Zinc Diffusion, .	12
Figure 2. Carrier Concentration as a Function of Zinc Diffusion,	13
Table III. Photovoltaic Data, Single Gap and Variable Gap Cells, .	15
Figure 3. Variable Gap Diode Characteristics,.	17
Figure 4. Spectral Response of Variable Gap Cells,	18
Figure 5. Open-Flow Gallium Phosphide Synthesis System,.	20
Figure 6. Gallium Phosphide Synthesized by Open-Flow System, . .	21
Table IV. Impurity Analysis of Starting Material and Syn- thesized Gallium Phosphide,.	22
Figure 7. Epitaxial Growth System Using Ga_2O_3 and Phosphorus Vapor,	26
Figure 8. Laue Pattern of Epitaxial Surface of Specimen M6211Bn,	27
Table V. Comparison of Epitaxial Surfaces,.	28
Figure 9. Iodine Transport of Epitaxial Surfaces,.	29

I. PURPOSE

The general objective of this Contract is to investigate the variable band gap structure $\text{GaAs}_x\text{-GaP}_{1-x}$, having a gallium phosphide surface grading to lower energy gap GaAs below the surface and containing a single junction. The practical objectives are to establish the optimums of diffusion, doping, depths, contacting and techniques to produce the most efficient devices of this structure. Inherent in this objective is the minimizing of sheet resistance, optimizing ohmicity of contacts, optimizing efficiency of the photovoltaic diode form, preservation of semiconductor lifetime and mobilities, and defining any advantageous characteristics - such as spectral response, high temperature performance, radiation resistance, or carrier injection characteristics.

II. ABSTRACT

Phosphorus diffusion schedules of 900°C-15 atmospheres, were found unsatisfactory and diffusion restricted to lower temperatures for two hours or less. A considerable number of variable gap and single gap cells were fabricated and tested. Studies of surface resistivity and carrier concentration as a function of zinc diffusion were carried out at temperatures of 500°C, 550°C, and 600°C. Photo parameters were improved; diode characteristics were uniformly good.

Chemical polishing of gallium arsenide wafers has been incorporated as a routine fabrication step. The etchant used for polishing was a sulfuric acid-peroxide solution.

Open flow synthesis of gallium phosphide using elemental phosphorus and Ga_2O_3 was successfully carried out. Dense growths of gallium phosphide needles were observed. Spectro-analysis indicate good purity. The needles are single phase gallium phosphide, of single crystal structure.

Epitaxial growth of gallium phosphide layers on gallium arsenide substrates was carried out by two methods. The first method, using Ga_2O_3 and elemental phosphorus in an open flow system is new for this purpose. The second method was by iodine transport in a closed system. Tentative results indicate both methods produced good epitaxial layers.

III. PUBLICATIONS, CONFERENCES & REPORTS

An article "Conversion of Gallium Arsenide to Gallium Phosphide by Solid State Diffusion" was published in the Journal of Applied Physics in the September, 1962, issue.

A conference was held at the Eagle-Picher Research Laboratories on September 25, 1962. Present were Mr. Phillip Newman of Fort Monmouth, New Jersey, Dr. J. R. Musgrave and Mr. Louis E. Stone of Eagle-Picher. Current progress was discussed, several suggestions of merit received, and guide lines for subsequent work agreed upon. The conference was very informative and constructive.

The I.R.E.-P.G.E.D. Meeting at Washington, D.C., October 27-29, was attended by Dr. J.R.Musgrave and Mr. Louis E. Stone of this laboratory. While there a brief conference with Mr. Phillip Newman was arranged, and samples with data accepted by him for delivery to Mr. Robert Yatsko, at Fort Monmouth, New Jersey.

Monthly Letter-Type Reports Nos. 4, 5, and 6 have been submitted promptly as scheduled.

The First Quarterly Technical Report was submitted on schedule, and mailed as per the Official Distribution List on schedule.

IV. FACTUAL DATA

A. INTRODUCTION:

The theoretical basis for the research performed on this contract has been discussed in previous reports⁽¹⁾. As outlined in the First Quarterly Technical Report, two forms of the variable gap structure have been investigated - (a) the deep variety, having gallium phosphide layers 10-microns or more deep produced by phosphorus diffusions of the order of 900°C, 20 atmospheres for several hours, and (b) the shallow structures of two to five microns depth, produced by diffusion of phosphorus at 800°C or less, 15 atmospheres, for shorter periods.

Fabrication of these structures into solar cell diode device form has been retained as it provides sensitive and more complete evaluation of the significant processing and contacting factors as well as the electronic characteristics. The fabrication steps have been fully detailed in a previous report⁽³⁾. Some refinements in fabrication have been made, and are discussed subsequently.

The cell geometry was studied, as reported in the First Quarterly Technical Summary Report⁽³⁾. The deep variable gap structure was found to suffer from compensation of the bulk material; poor photovoltaic parameters were observed. Further clarification of this problem is discussed subsequently.

The shallow variable gap structure has been the subject of further study during this period. This form does not suffer serious deterior-

ation of bulk properties during phosphorus diffusion and was used for the zinc junction studies.

The formation of a good p-n junction within the gallium phosphide layer appears to be the key to achieving a significant improvement in the variable gap device, and realization of the potential advantages thereof. Hence, studies were carried out of carrier concentration as a function of temperature of zinc diffusion in the variable gap structure. In the course of these studies, reproducibility has been very good, and several variable gap cells of more than 6 percent efficiency were made.

One significant factor has become apparent. The rate of diffusion of zinc in gallium phosphide is greater than in gallium arsenide. Thus it is difficult to obtain a junction more shallow than the bottom of the gallium phosphide layer, and at the same time achieve high carrier concentration. To evaluate this difficulty, and to contrast the effects of a gradient gallium phosphide concentration with an abrupt gallium phosphide - gallium arsenide transition, some effort was planned on epitaxial layers. Gallium phosphide for this purpose has been synthesized by an open-flow system somewhat similar to that described by Bodi⁽⁴⁾. Results were quite good and are described.

Epitaxial layers were grown with this material as source gallium phosphide, using the iodine transport system. Although x-ray proof of structure and identity has not as yet been completed, tentative microscopy indicates true epitaxial growth of single crystal material.

Epitaxial growth by a method similar to the synthesis method was carried out. To our knowledge, this method has not as yet been reported in the literature. Tentative microscopy indicates a gallium phosphide layer; x-ray structure is single crystal. Direct x-ray identity as gallium phosphide has not been completed yet.

B. Fabrication:

(1). Sequence.

Essential fabrication steps for both single gap and variable gap structure are outlined in Table I.

TABLE I

Cell Fabrication Steps and Sequence.

	<u>Variable Gap</u>	<u>Single Gap</u>
1. Dice material to appropriate size.	X	X
2. Lap with 600-Grit Compound to clean saw debris.	X	X
3. Diamond polish to optical finish.	X	X
4. Chemically polish in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ etchant.	X	X
5. Rinse thoroughly in Deionized water and dry.	X	X
6. Seal in evacuated, purged ampoule with appropriate phosphorus charge and diffuse.	X	
7. Clean chemically in HF or HI acid, rinse, dry.	X	
8. Diffuse zinc to form junction.	X	X
9. Mask surface with Krylon, lap bottom surface heavily.	X	X
10. Electro-plate nickel on bottom surface.	X	X
11. Lap edges heavily, dissolve Krylon, clean, rinse, and dry.	X	X
12. Mask top surface, sputter platinum collector on top.	X	X
13. Apply solder coating to top and bottom contacts.	X	X
14. Cell ready for evaluation.		

(2). Chemical Polish.

Diamond polishing of wafers has regularly been used to produce a flat, highly polished surface. Etching of such surfaces has indicated high densities of dislocations, and made attractive a chemical polishing step to remove such damaged layers, while retaining the flat, polished surface. A satisfactory procedure was developed by adapting the technique described by Sullivan & Pompliano⁽⁵⁾. Wafers are randomly rotated in a solution of 70 percent H_2SO_4 , 15 percent H_2O_2 (30%) and 15 percent H_2O for periods of about 30 minutes. The resulting surfaces are undamaged, clean and flat. This procedure has improved the reproducibility of the diffusion process significantly.

(3). Phosphorus Diffusion.

Red phosphorus, semi-conductor grade, from the American Agricultural Chemical Company is used. Wide variations in impurity concentrations were found from batch to batch by spectro analysis. Table II illustrates spectro-analyses of the two extremes.

TABLE II

Spectro-Analysis of Phosphorus Lots, Parts Per Million.

	<u>Si</u>	<u>Pb</u>	<u>Mg</u>	<u>Fe</u>	<u>Al</u>	<u>Cu</u>	<u>Ca</u>	<u>Sn</u>	<u>Ni</u>
M6207BQ	40.	1.	5.	1.	5.	1.	1.	---	----
M6206CH	500.	5.	30.	10.	10.	2.	10.	30	5

Attempts were made to further purify Lot Mb207 BQ by multiple sublimation. Spectro-analysis indicated little or no improvement.

Hence selected best grade material was used without further treatment. The impurity levels involved here are considered one of the major difficulties in fabricating high efficiency variable gap structures. Phosphorus diffusion was carried out in evacuated, heavy-wall quartz ampoules. The phosphorus charge, calculated as P_4 , to produce the selected pressure at the desired diffusion temperature was placed at one end of the ampoule, the specimen wafers at the center, and after 5 cycles of evacuation-purging with an inert gas, the ampoule sealed off under approximately 1-micron vacuum. After diffusion, the ampoules were moved to the end of the hot zone, and the phosphorus deposited at one end by selective cooling. This end was sawed off in opening the ampoules.

Diffusion schedules fall in two general categories, 800°C - 15 atmospheres for periods of one to three hours, and 900°C - 20 atmospheres for periods of two to fifty hours. The former produces "shallow" gallium phosphide layers of the order of 3-microns thick, the latter "deep" layers of 10 to 20-microns thick, as defined by etch-resistance and staining techniques.

Wafer surfaces regularly were bright and clean, with no erosion, and little if any stains or filming. Rinsing with HF was regularly done to remove any possible films prior to zinc diffusion. Cross sections of such variable gap structures, when observed under polarized light at 500X, indicate an homogeneous layer, of orange color, varying in thickness with diffusion schedules.

(4). Zinc Diffusion.

Zinc diffusion is routinely done in fused silica boats, in a hydrogen (reducing) atmosphere. The variable gap and/or single gap wafers are placed centrally, with small pieces of high purity zinc at each end of the boat. The boat is held outside the hot zone of the split-type tube furnace until stabilized at the desired temperature, then moved manually to the exact center of the heated tube, and after the desired diffusion time, moved again to the cool, downstream end. The tube and boat are removed entirely from the furnace and evaporative water cooling used for rapid cooling. This is done in cognizance of the work by Gershenson, et. al.,⁽⁶⁾ who advise quench cooling to prevent formation of precipitation site trapping centers. Purging is done with argon; thorough outgassing with moderate flow hydrogen is done before inserting the boat in the hot zone, at which time hydrogen flow is reduced almost to nil; following diffusion, high rate flow is done to sweep zinc vapors out.

(5). Contacting.

Electroplated nickel contact is made to the bottom (n) material. It is plated at a rate of approximately 25 ma/cm² from the hydroxide (basic) solution usually used for electroless plating.

Sputtered platinum collector contact is made to the top surface, as a 1-mm wide stripe lengthwise of the wafer.

Both contacts when applied, show slight non-ohmicity and some series resistance. Coating with 60-40 solder eliminates both, and

produces a good contact - as illustrated subsequently by diode characteristics. More sophisticated contacting, such as alloyed aluminum or lead is possible, and would no doubt produce some improvement in efficiency, but would introduce additional complexities to the processing.

C. STUDIES AND EVALUATION:

(1). General.

Testing techniques and procedures are standard and current with the present state of the art, and designed to correlate with other laboratories to the closest practical degree. The following outlines the methods used.

- (a). Resistivity is measured using four terminal, potentiometric method, with current contacts isolated and widely spaced from voltage drop terminals.
- (b). Four-probe resistivity of surfaces is done using conventional 4-probe head and technique.
- (c). Two-probe resistivity or resistance per square measurements are made on cell surfaces using special semi-blunt points to prevent surface puncture.
- (d). Photo parameters are measured using a Hewlett-Packard Model 425 Micro-Micro Ammeter. I_{sc} is measured as the voltage drop across a precision 1-ohm resistor.
- (e). Light measurements are made in sunlight using an Eppley Pyroheliometer, collimated against reflected light. When laboratory testing is required, a similar calibrated cell is used to adjust an RFL-2 light to give equal I_{sc} current through a 1-inch water filter.
- (f). Spectral response is measured with a Bausch & Lomb Spectrophotometer of the grating type.
- (g). Temperature performance is measured in a special Blue-M regulated oven, with built-in instrument wiring, capable of close, automatic regulation to over 200°C.

- (h). Diode characteristics are measured using the curve-tracer technique, and a Tektronix Model 535 Oscilloscope.
- (i). Cross section device geometry is done using an electro-etch stain technique developed in our laboratory, in conjunction with a Unitron Microscope fitted with built-in camera.

(2). Carrier Concentration and Junction Depth Studies.

The formation of good p-n junctions requires carrier concentrations of the order of 10^{20} atoms/cc, and depths of the order of 1-micron. These requirements have led to zinc diffusion temperatures as low as 500°C to obtain minimal depths, at which temperature it is difficult to obtain the required high concentrations.

To define the equilibrium concentration obtainable, studies of surface resistivity, ohms per square, as a function of diffusion time were carried out on variable gap structures of the shallow variety, for temperatures of 500°C, 550°C, and 600°C. In each case, four to six wafers, including one virgin gallium arsenide control blank, were diffused, using identical techniques, for different times at a certain temperature. Many 2-probe measurements of each wafer were made. The scatter of these measurements was very small, of the order of ten percent maximum for a single wafer, and five percent or less between wafers. The average of these measurements are plotted in Figure 1, for 500°C, 550°C, and 600°C, respectively. Subsequently trials were made to check the reproducibility of the technique. In all cases, reproducibility was good, within the measurement scatter, with similar material.

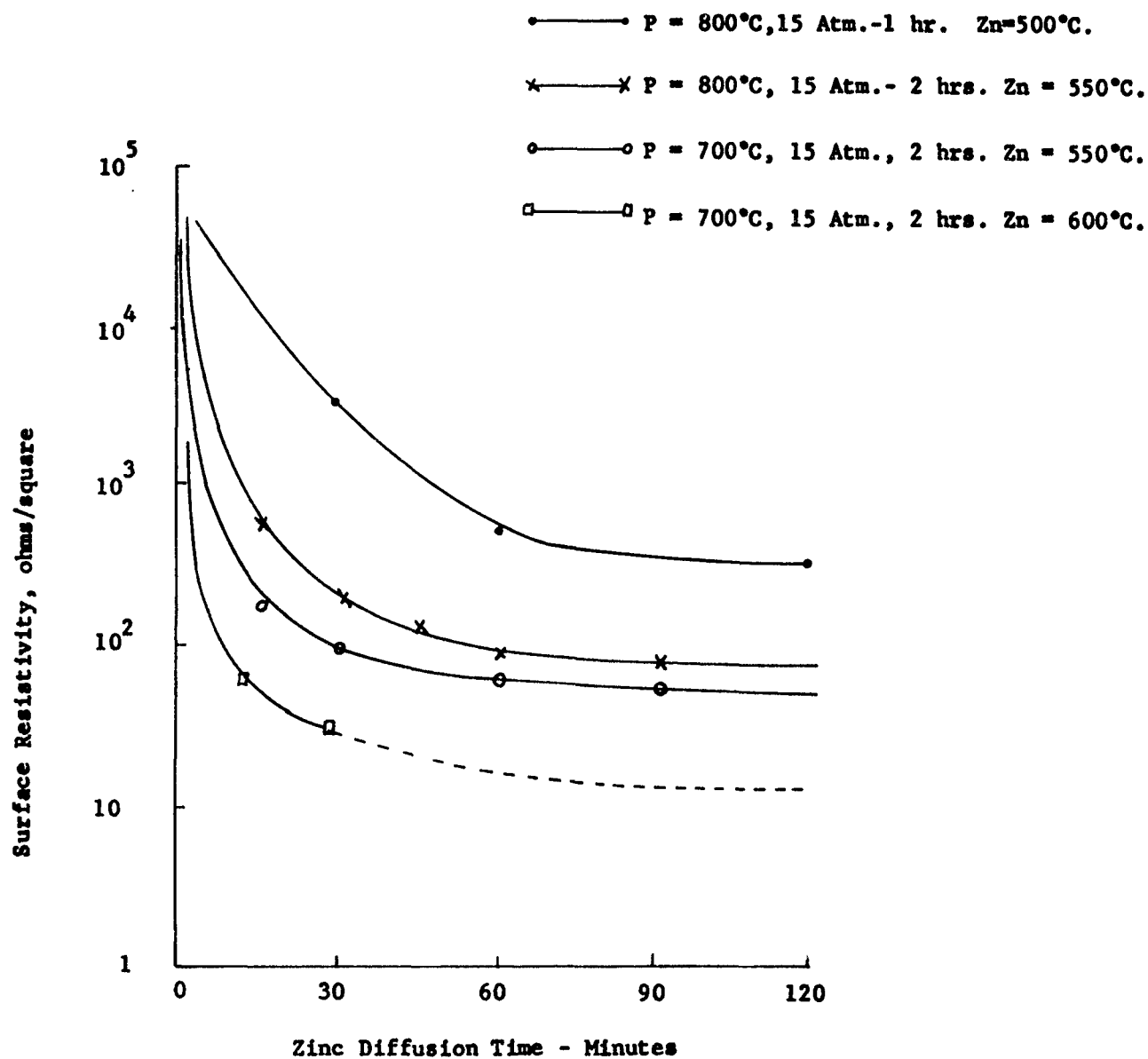


Figure 1. Surface Resistivity as a Function of Zinc Diffusion.

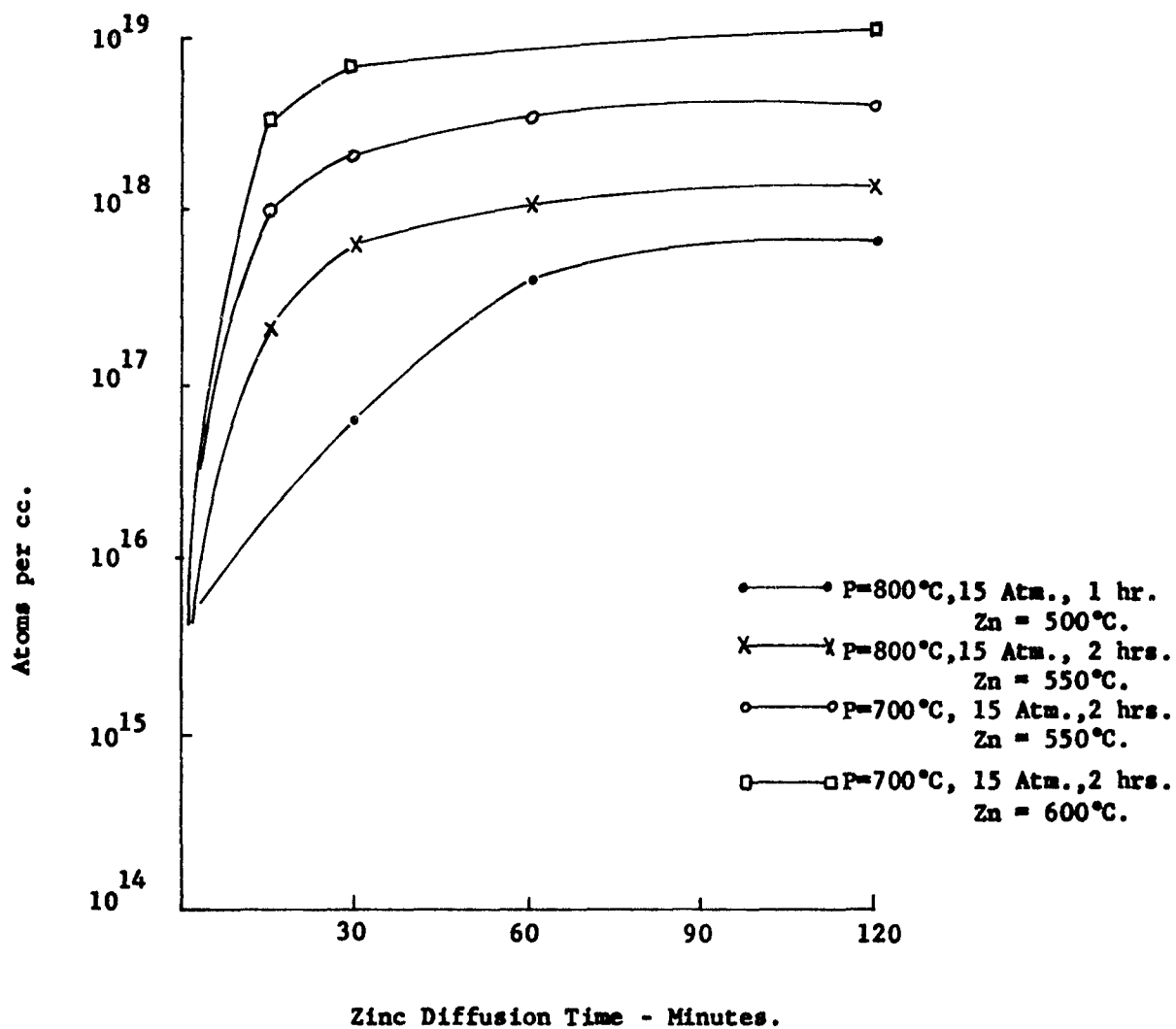


Figure 2. Carrier Concentration as a Function of Zinc Diffusion.

The surface carrier concentration derived from the surface resistivity are indicated in Figure 2.

The surface carrier concentration is observed to increase with temperature, and equilibrium concentrations approaching $10^{19}/\text{cm}^3$ are attained at 600°C. Typical variable gap cells of 700°C, 15 Atmospheres - 2 hours, when zinc diffused 600°C - 10 minutes, exhibit gallium phosphide layer of the order of two or three microns thickness with the p-n junction slightly below the bottom of the gallium phosphide layer. Effort to increase the carrier concentration by extending the zinc diffusion time, moves the junction deeper into the gallium arsenide, with noticeable deterioration of photo parameters.

(3). Photovoltaic Parameters.

During the period of this report, a considerable number of variable gap and single gap control cells were fabricated. Since primary considerations were in determining junction parameters of the variable gap cells, many were sectioned, stained, etc. Typical specimens of the groups were evaluated as solar cells, and such testing was done in sunlight. Typical data are listed in Table III.

TABLE III

Photovoltaic Data For Single Gap and Variable Gap Cells

Cell Number	Phosphorus Diffusion	Zinc Diffusion	V _{oc} Volts	I _{sc} Ma/cm ²	Eff _{mp} Percent	V _L Volts	Sunlight Test Intensity(mw)
429	800°-15-1 hr.	600°-10 Min.	0.72	8.5	4.4	0.56	92.
431	800°-15-1 hr.	500°-30 "	0.70	9.1	4.5	0.52	87.6
459	800°-15-2hrs.	550°-90 "	0.69	10.5	4.7	0.52	92.1
466	700°-15-2hrs.	600°-10 "	0.79	12.1	6.4	0.62	92.2
472	700°-15-2hrs.	600°-30 "	0.72	6.8	3.6	0.50	83.
448	- - - - -	550°-60 "	0.74	10.8	5.4	0.56	93.1
450	- - - - -	550°-60 "	0.75	9.	5.0	0.60	91.2
462	- - - - -	550°-15 "	0.76	15.5	5.0	0.44	91.2
465	- - - - -	600°-10 "	0.80	10.5	5.5	0.58	90.3
468	- - - - -	550°-30 "	0.80	10.5	5.6	0.62	91.2

It is significant to note that the variable gap cells listed above have gallium phosphide layers of 2-microns or more, with p-n junctions averaging 1-micron deeper, yet V_{oc} of 0.79 and Eff_{mp} of 6.4 percent were attained. These values are equal to - or better than - the equivalent single gap cells, with junction depths of 1-micron or less.

Gradual improvement in V_{oc}, V_L, and Eff_{mp} has been observed. An increasing percentage of cells fabricated at the optimum diffusion schedules are of good efficiency; the number of defective units decreases. Significant factors include improved, higher mobility material, surfaces nearer the ideal, and improvements in techniques.

(4). Diode Characteristics.

The variable gap cells exhibit good diode characteristics. Typical diode curves are illustrated in Figure 3. The reverse voltage breakdown point is in excess of 4.5 volts, with very small leakage currents. Forward threshold voltage is regularly about 0.6 volts or more. The dynamic forward resistance of these cells range from 0.6 to 1.0 ohm, indicating low contact resistance, and appears satisfactorily low. General diode characteristics are equal to, or better than, equivalent single gap diodes.

(5). Spectral Response.

Spectral response of recent, shallow type, variable gap cells is observed to be very broad, as illustrated in Figure 4. The response is typically 60 percent of maximum at 0.5 micron wavelength with a broad, flat characteristic from 0.725 micron to 0.85 micron, dropping sharply to nil at about 0.925 micron. The short wavelength response is sensitive to junction depth, becoming sharply peaked at 0.85 micron as the junction is made deeper in the gallium arsenide bulk.

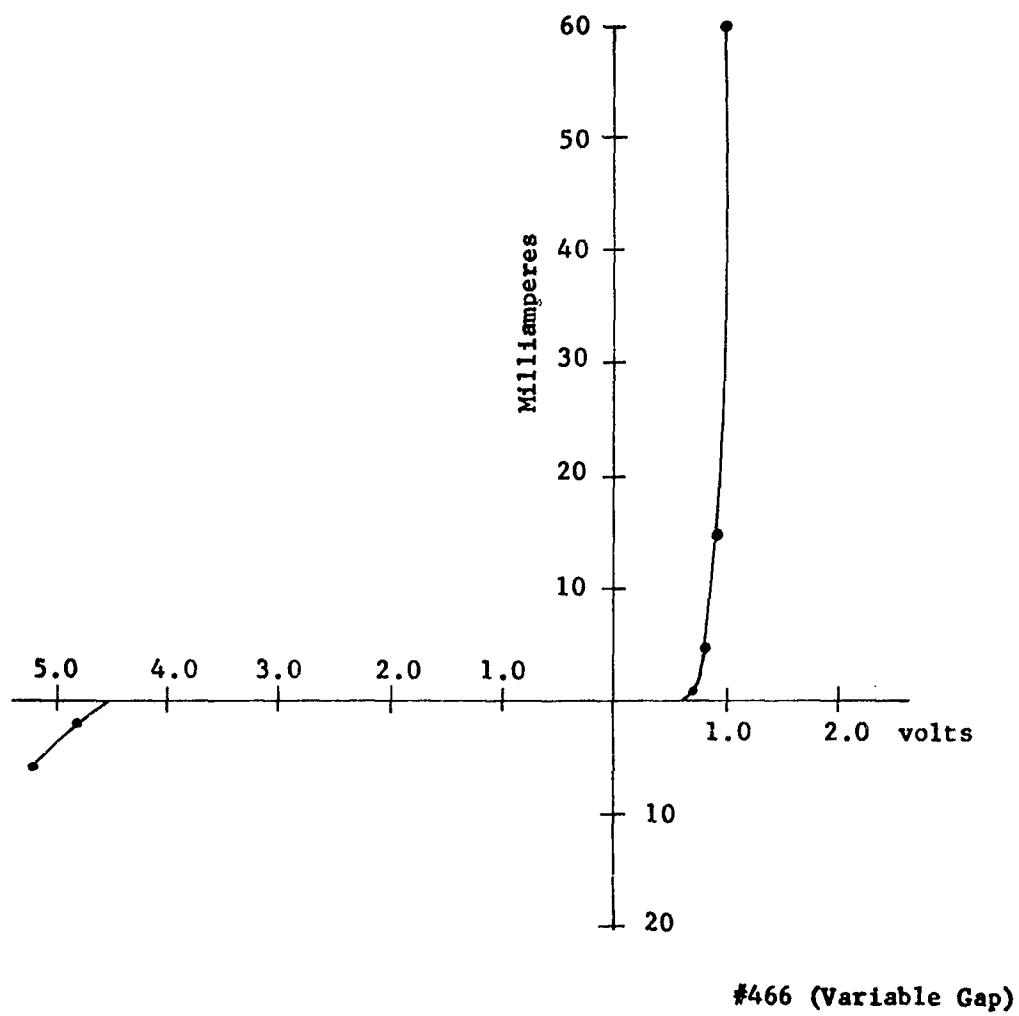


Figure 3. Variable Gap Diode Characteristics.

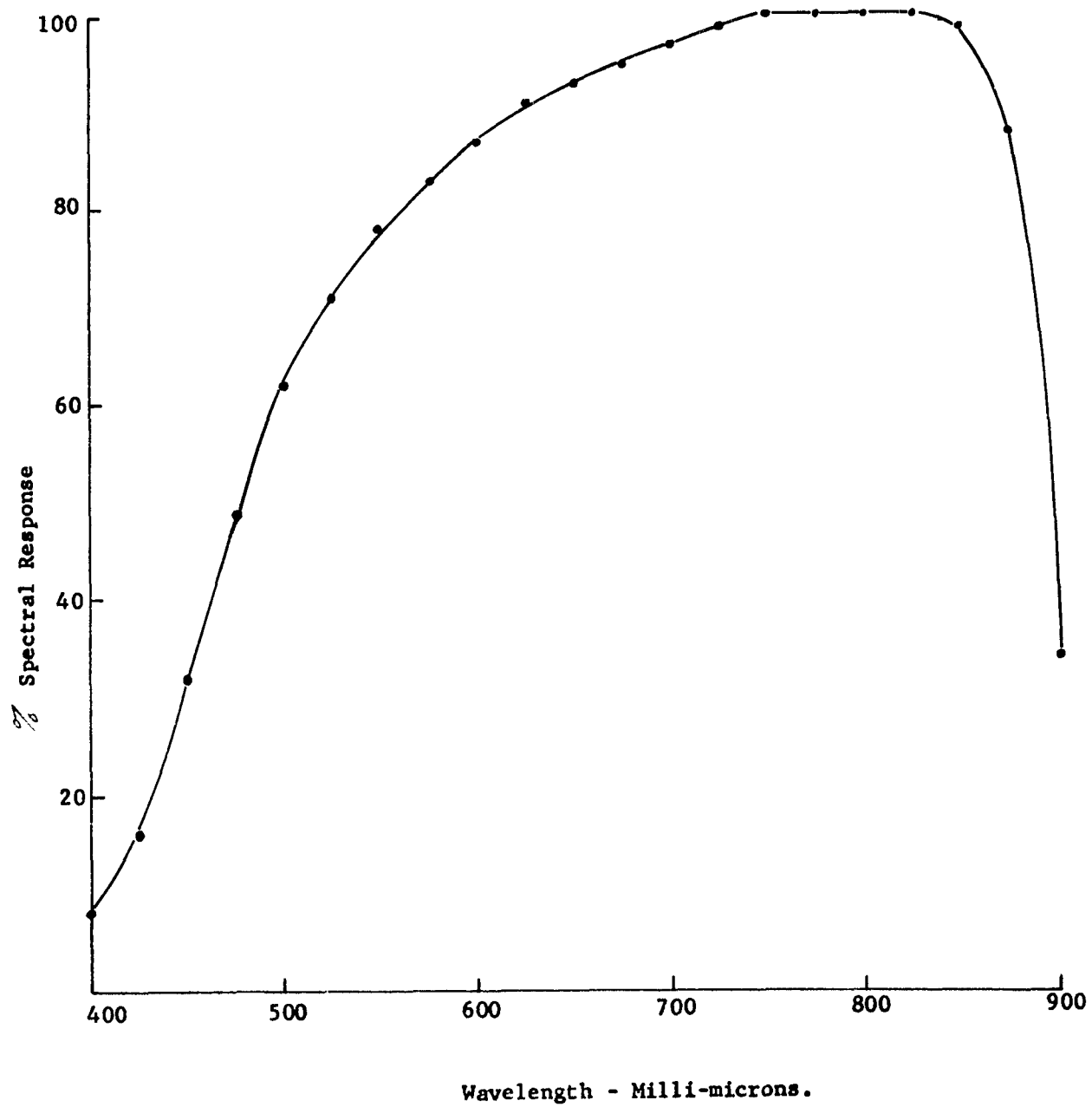


Figure 4. Spectral Response of Variable Gap Cell.

D. Gallium Phosphide Synthesis.

Initial guide lines of the investigation included the comparison of variable gap, diffused type structures with step-type structures of gallium phosphide on gallium arsenide, in which little or no grading of the transition region occurs. The course of the investigation has reached the point where such comparison may be very useful and informative. Epitaxial growth appears the logical method of achieving the step-type structure. Tentative efforts at synthesizing gallium phosphide from elemental gallium and phosphorus were successful and an ingot, essentially single crystal, was made by synthesis-melt growth in a high pressure system⁽³⁾. Subsequent work reported in the literature by Bodí⁽⁴⁾ appeared attractive as a method of synthesis, where the end product is not required to be massive single crystal ingots, as is indeed the case here. Thus, gallium phosphide was synthesized in a system modeled after the Bodí method, as source material for epitaxy.

The general synthesis system is illustrated in Figure 5. Phosphorus is sublimed at 400°C in one zone of a multiple-zone furnace, and carried by dry hydrogen gas over a charge of Ga_2O_3 at 900°C in a second zone of the furnace. Hydrogen flow rates are minimal. The exit of the quartz reaction tube is enclosed in a dry ice cold zone to trap vapor reaction products. Exhaust gas is passed through a potassium permanganate trap and exhausted or burned. Reaction time is of the order of several hours. Minimal reaction zone temperatures and hydrogen flow rates encourage the growth of needle structure growth. Figure 6 illustrates the gallium phosphide product. Recovery of gallium as gallium phosphide in the initial runs was approximately 75 percent.

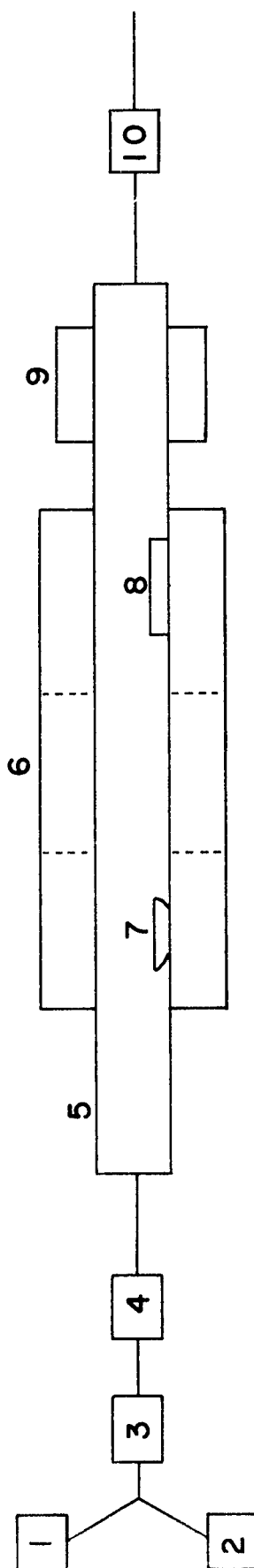


Figure 5. Open-Flow Gallium Phosphide Synthesis System.

1. Argon
2. Hydrogen
3. Acetone - Dry Ice Trap
4. Molecular Sieve
5. Quartz Tube
6. 3-Zone Furnace
7. Phosphorus Charge
8. Ga_2O_3 Charge
9. Dry Ice Condenser
10. Bubbler

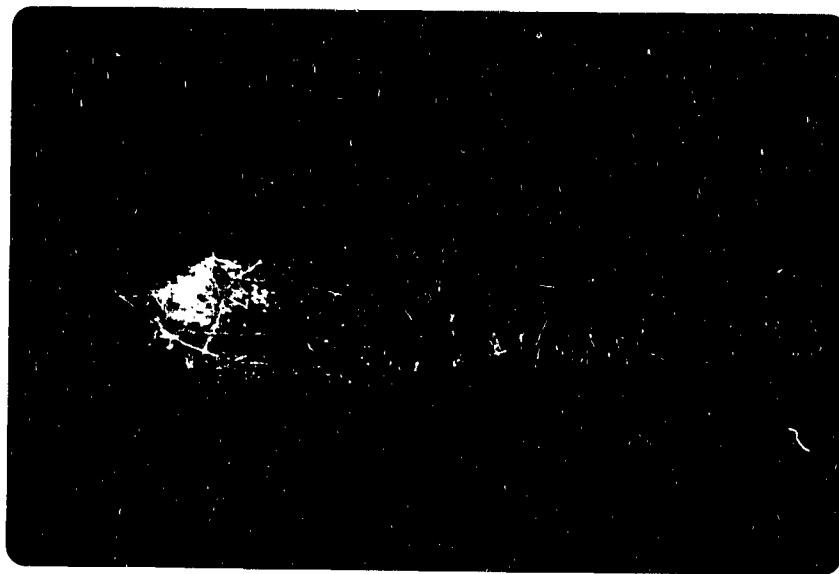


Figure 6. Gallium Phosphide Synthesized by Open-Flow System.

The surface of the gallium phosphide was a dense growth of large needles, microscopically symmetrical and highly transparent, of yellow-orange color. Beneath the needle was a mat of gallium phosphide powder. Removal of both the needles and mat revealed an adherent coating of gallium phosphide on the fused silica boat. Samples of starting materials, needles, and powder scraped from the boat were analyzed by emission spectroscopy. Impurity data of these specimens are tabulated in Table IV. The residual powder encrusting the boat was sintered for ten hours at 1000°C and analyzed for impurity content. These data are included.

TABLE IV

Impurity Analysis of Starting Materials and Synthesized
Gallium Phosphide.

<u>Specimen</u>	<u>Identity</u>	<u>Si</u>	<u>Pb</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>Ca</u>	<u>Cu</u>	<u>Sn</u>	<u>Total PPM</u>
Lot 137-1	Ga ₂ O ₃	-	<.07	-	-	.15	.66	.34	<.1	1.32
M6207 BQ	Phosphorus,	40.	<1.	1.	5.	5.	1.	1.	-	54.00
M6209 BS	GaP Needles,	.5	<.1	1.	.2	-	1.	-	-	2.80
M6209 BT	GaP off Boat,	100.	<.1	3.	.5	-	2.	-	-	105.60
M6209 BU	GaP off Furnace Tube,	100.	<.1	.5	.5	-	.5	-	-	101.60
M6211 AA	Residual GaP Sintered*	5.	-	-	10.	3.	10.	2.	-	30.00

NOTE: * = Residual GaP chg. sintered 10 hours, 1000°C in Hydrogen ambient atmosphere.

The data indicate some of the impurities from the Ga₂O₃ and phosphorus is carried over in the gallium phosphide, but especially in the needle growth, an impurity segregation process is evident. High silicon contamination from the fused silica boat is apparent; this may be alleviated by retaining a gallium phosphide covering on the boat.

Specimens of the needles were submitted for x-ray diffractions study (7). The Laue patterns indicated very good single crystal structure with no indication of mixed phases. The diffraction powder study is summarized in the following report.

A single needle-shaped crystal was selected for a single crystal pattern and the remainder was ground for a powder pattern. The results are tabulated and compared with two earlier samples (M6109AQ and M6204AB).

The powder pattern of M6209DM was measured and both the inter-planar spacings (d values) and the edge length of the unit cell (a_q) were calculated. Gallium phosphide has a diamond structure similar to zinc sulfide in the sphalerite form. Since gallium and phosphorus ions have different diffracting properties certain planes give diffraction lines which do not produce lines in a diamond structure comprised of only one kind of atoms. These planes are the (200), (222), (420), (600), and the (622). In several instances these lines are very weak and the inability to measure them does not indicate their absence.

The pattern of the needle-shaped crystals contains a low theta line at about 3.24 \AA° which has been observed on previous samples but has not been entirely explained. If arsenic were present it could be accounted for as a second phase, perhaps as a surface layer, of a gallium arsenophosphide solid solution. If arsenic is completely absent two possible explanations can be suggested: The grinding of the sample to a powder was accompanied by a strong odor of "matches" and it is possible that traces of mixed oxide-phosphide account for the extra line. The other possibility is that the mechanical work done in grinding resulted in the crystal being partially converted or "smeared" to an unstable or strained condition which gives rise to this extra line. Opposed to this, however, is the fact that the lines are not broadened.

The unit cell values reported in the literature when compared with

those measured in this laboratory are in reasonably good agreement. However, since the materials with which we are working are perhaps purer than those available to previous investigators the actual values and the differences in results are of interest. The small difference becomes significant when the influence of impurity atoms on unit cell dimensions is considered.

Wyckoff gives a value of 5.436 \AA but the literature reference is not given. The recent publication of Giesecke & Pfister (Acta Crystallographica, 11, 369, (1959) gives a value of 5.4505 \AA which is based on the single (531) plane. Quoted in the G & P paper is a 1926 value of 5.447 due to Goldschmidt. Many factors play a part in determining the final values assigned to a unit cell dimension in addition to the sample. Tabulated below are the measured values obtained here on three gallium phosphide samples and data on the determinations and comparisons with literature values:

Sample a_0		
M6109 AQ	5.4502	Weighted mean of all lines (accepted)
M6204 AB	5.4447	Weighted mean of all lines
	5.4508	Weighted mean of doublets (accepted)
M6209 DM	5.4495	Weighted mean of all lines (accepted)
	5.4519	Weighted mean of doublets
	5.4466	Refined by a $\sin^2 \theta$ method
Literature:	5.4505	Giesecke and Pfister
	5.447	Goldschmidt
	5.436	Wyckoff

NOTE: It appears that a value of a_0 in the order of $5.4500 \pm .0005 \text{ \AA}$ is very close to the true value.

Tentative measurements of resistivity of these needles were made. Contacting was by silver paste on copper laminate mounts. This contacting indicates fairly uniform resistivities of approximately $1 \times 10^6 \text{ ohm-cm}$. The resistivities were not greatly sensitive to light.

E. Epitaxial Growth.

Based on the excellent results in synthesizing gallium phosphide and observations of the dendritic needle growth, use of the same general system appeared promising for epitaxy. The general system is illustrated in Figure 7. Principal modifications include:

- (a). A fused silica boat, partitioned, to place the Ga_2O_3 closely adjacent to the gallium arsenide substrates, yet separate to insure growth from the vapor phase only.
- (b). A heat sink arranged to insure the substrates being the coolest surface in the vicinity of the synthesis area.
- (c). Provisions to move the entire boat into and out of the hot zone.
- (d). Appropriate instrumentation for temperature measurement.

The synthesis-growth operation was carried out in a 30 mm I.D. fused silica tube, housed in a multiple zone furnace. Substrate wafers and a few grams of Ga_2O_3 were placed in the separate compartments of the rectangular boat but retained outside the furnace while initial heating was done. A few grams of red phosphorus was placed in a silica boat and retained outside the furnace until stabilized temperatures were accomplished. The system was purged with dry argon and hydrogen. The heat sink was adjusted to obtain approximately 850°C substrate temperature. The phosphorus was inserted in the 400°C zone and growth carried out under very low hydrogen flow rate for two hours. The phosphorus boat was then retracted, hydrogen flow rates increased and the furnace turned off for cooling.

A yellow powder deposit was observed on two of the three specimens. It was easily wiped off and did not appear to erode or damage the surfaces. Surfaces were smooth and lustrous with little evidence of staining and appeared grey in color to the naked eye.

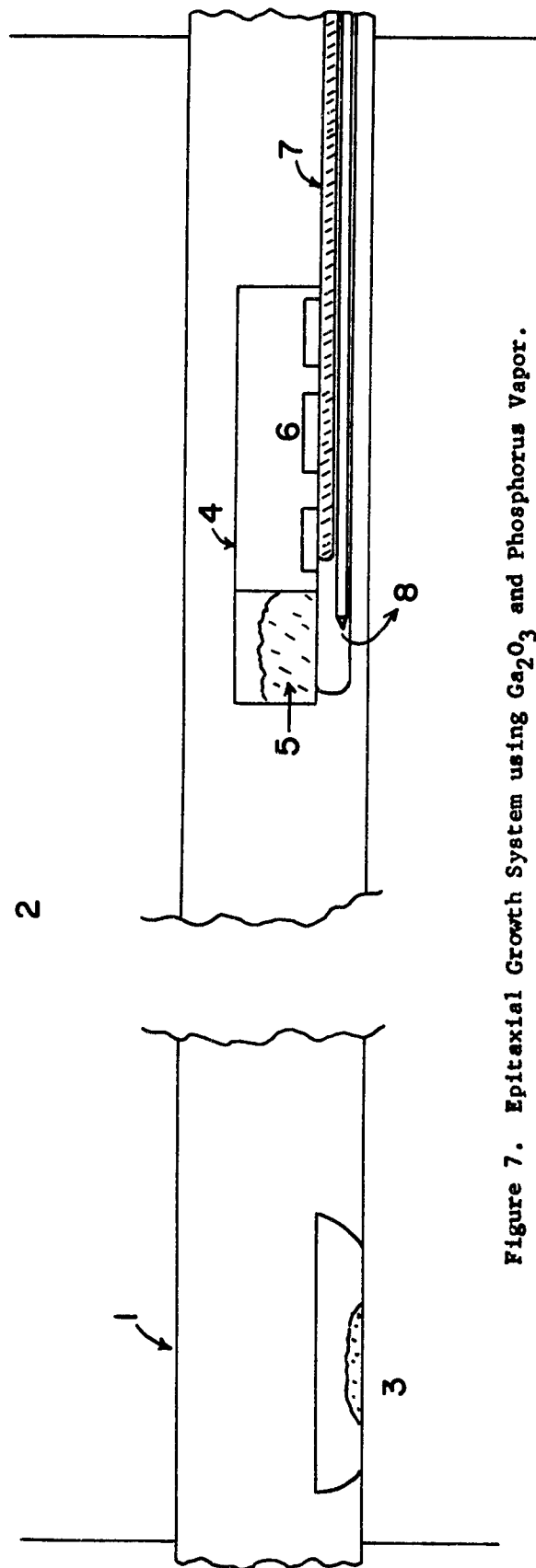


Figure 7. Epitaxial Growth System using Ga_2O_3 and Phosphorus Vapor.

1. Quartz Tube
2. 3-Zone Furnace
3. Phosphorus Charge
4. Quartz Boat Welded on Quartz Tube
5. Ga_2O_3 Charge
6. GaAs Wafers
7. Copper Heat Sink Inside Quartz Tube
8. Thermocouple Inside Quartz Tube

Microscopic examination was made of a cross sectioned wafer. An orange-colored layer was observed. Rigorous etching in $\text{KOH-H}_2\text{O}_2$ did not significantly affect this layer although the underlying gallium arsenide was severely attacked. A specimen, M6211BN, was submitted for x-ray determination of structure. The Laue pattern obtained is illustrated in Figure 8. Exposure was made at approximately 15° from perpendicular to the surface and produced the typical 1:1:1 three-fold symmetry. No evidence of mixed phases was observed. Since the unit cells dimensions of gallium arsenide and gallium phosphide are so similar, positive identity of gallium phosphide requires direct comparison of halves of the same wafer, one with gallium phosphide growth.

Based on microscopic examination, however, the identity as gallium phosphide appears rather certain.



Figure 8. Laue Pattern of Epitaxial Surface of Specimen M6211BN.

An exploratory trial was made of epitaxial growth of gallium phosphide on gallium arsenide substrates, using the previously described gallium phosphide needles as source material, and the iodine transport method. The substrates, source, and elemental iodine were sealed in a quartz ampoule under vacuum. The ampoule was placed in a multiple-zone furnace and a suitable temperature gradient imposed. Figure 9 illustrates the salient features of the experiment. Substrate temperature was 700°C, source temperature was 850°C, and time of growth extended to two hours. Cognizance was taken that this schedule would involve growth of greater than the desirable thickness. Two specimens were used; one was broken in opening the ampoule.

Microscopic examination of the other indicates growth was accomplished. A yellow-orange translucent layer is observed under polarized light. Depth measurements and x-ray determinations have not, as yet, been completed.

Some electronic measurements have been made. Some data comparing the synthesis-growth and iodine transport methods are presented in Table V. Since initial efforts are represented in each case, and both efforts deliberately arranged to produce rigorous effects and relatively thick layers, this data should be considered in that light.

TABLE V

Comparison Data of Epitaxial Surfaces.

Parameter	Synthesis Grown	Iodine Transport
Starting Material Resistivity,	.17 ohm-cm	0.005 ohm-cm
Starting Material Type,	"N" - Moderate	Strong "P" type zinc doped.
Ending type of Surface,	"N" - Moderate	P-type - Moderate
Starting Surface Resistivity	3×10^6 ohms per square	5×10^3 ohms per square
Ending Surface Resistivity	7×10^4 " " "	8×10^4 " " "

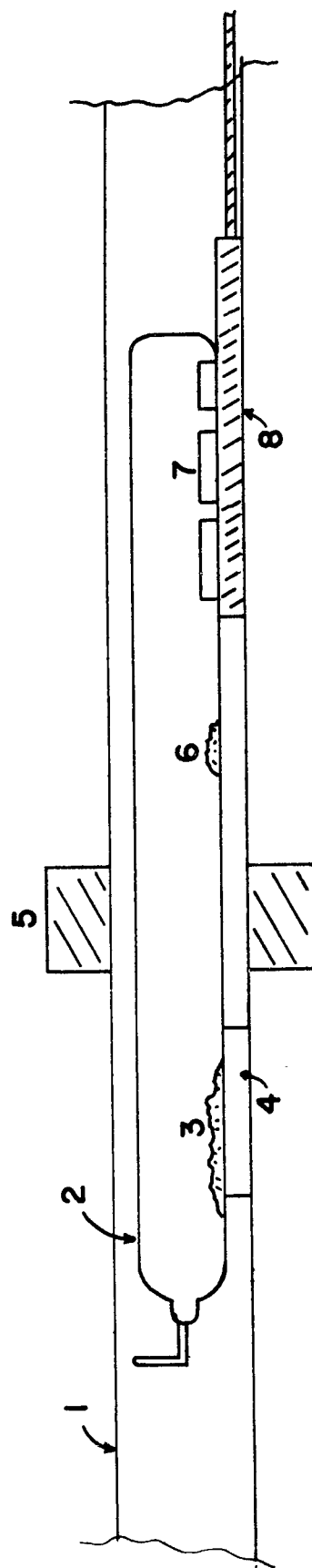


Figure 9. Iodine Transport Epitaxy System.

1. Quartz Tube
2. Sealed Ampoule
3. Gallium Phosphide Charge
4. Quartz Support
5. Insulating Ring
6. Iodine
7. Gallium Arsenide Wafers
8. Copper Heat Sink

V. SUMMARY AND CONCLUSIONS

Current progress has defined the surface carrier concentrations obtained as a function of zinc diffusion schedules. Refinement in techniques make it possible to reproduce these values as desired. Improvement in surface preparation by chemical polishing eliminates disturbed or damaged layers resulting from sawing and mechanical polishing. Some improvement in variable gap efficiencies as solar cells has been achieved. The mechanics of gallium phosphide synthesis by an open-flow method has been studied. A system and parameters capable of reproducibly synthesizing this material have been described. Impurity levels are principally dependent upon phosphorus purity.

Stoichiometry and crystalline structure of the synthesis product is good; the material is suitable for bulk gallium phosphide growth from the melt or as a source for epitaxy.

Tentatively, epitaxial growth by two dissimilar methods was accomplished. One method, similar to the synthesis technique, is an open flow system. Principle disadvantage appears to be a slightly higher substrate temperature. The second method, using iodine transport, allows low substrate temperatures.

VI. FUTURE STUDIES

Included in plans for the next period are the following:

Continued improvement in the diffused, graded band gap structures by efforts to optimize the phosphorus diffusion schedules, increase the carrier concentration while maintaining shallow depth junctions, and decreasing the levels of contaminating impurities in the phosphorus.

Fabrication of epitaxially grown structures with step-type transition to gallium arsenide and the formation of p-n junctions therein.

Fabrication of epitaxial structures and a brief effort to produce gradient transition by subsequent heat treatment.

Evaluation of the diffused, gradient structure for light emission characteristics under forward bias conditions.

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VIII. PERSONNEL

Engineering Time Expended from August 1, 1962 to November 1,
1962.

Louis E. Stone,	416 Hours
George N. Webb,	496 "
Richard H. Fahrig,.	20 "
Harold L. Allen,.	36 "
William A. Ames,.	19 "
S. J. Roderique,.	88 "
	<hr/>
Total Hours,	1,075 Hours

LES/tp.

AD _____ Accessories No. _____ UNCLASSIFIED

The Eagle-Picher Company, Chemical & Metals Division, Miami, Oklahoma.
VARIABLE ENERGY GAP DEVICES
L. E. Stone, G. N. Webb, J. R. Musgrave

Second Quarterly Technical Report - August 1, 1962 to November 1, 1962.
33 pp - Illustrations - Graphs
Signal Corps Contract Nr. DA-36-039-SC-89106

Gallium phosphide variable gap devices made. Diffusion of zinc at low temperatures and carrier concentrations. Photo voltaic parameters, diode characteristics and spectral response. Gallium phosphide epitaxy on Gallium Arsenide by two methods - initial results.

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Energy Gap

Devices

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Arsenide De-

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3. Photovoltaic Devices

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